California Regional PM_{10} and $PM_{2.5}$ Air Quality Study (CRPAQS)

Statement of Work – CRPAQS Data Analysis Task 6.2
FACTORS LIMITING THE FORMATION OF SECONDARY NITRATE AND SULFATE

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Sonoma Technology, Inc.

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Introduction

Ambient concentrations of particulate matter (PM) exceed health-based air quality standards in central and southern California. The development of effective emissions control strategies to mitigate this problem requires an understanding of the chemical and physical phenomena that cause high air pollution concentrations. One factor associated with high PM levels is high levels of secondary nitrate and sulfate during winter air pollution episodes. Improved characterization of the factors influencing, and especially those limiting, the formation of secondary nitrate and sulfate is likely to advance the understanding of the phenomena that cause unhealthy air quality.

Analysis of the chemical composition of PM during winter pollution episodes indicates high levels of nitrate, modest levels of sulfate, and levels of ammonium sufficient for these two anions to exist primarily as ammonium nitrate and ammonium sulfate in atmospheric aerosols. The nitrate and sulfate found in PM are believed to be secondary because there are no known primary emission sources with significant emission rates of these compounds and because there are known chemical reactions that lead to their formation in the atmosphere. The chemical formation of pathways are complex and believed to be dependent on the ambient concentrations of gaseous precursors (VOC, NO_x, NH_3, HNO_3, and SO_2) and oxidants (ozone and H_2O_2), and meteorological factors such as temperature, humidity, fog, precipitation, sunlight, transport winds, and vertical mixing characteristics. For example, the principal daytime nitrate formation pathway involves sunlight- and VOC-driven oxidation of NO emissions in the presence of ozone to form NO_2 which is further oxidized to nitric acid (HNO_3), which then reacts with gaseous ammonia (if available) to form ammonium nitrate if favorable temperature and relative humidity conditions prevail. At night, the NO_x oxidation pathway involves conversion of NO to NO_2 and NO_2 to gaseous NO_3 if sufficient ozone is available, followed by conversion of NO_3 to N_2O_5 if NO levels are sufficiently low, followed by N_2O_5 conversion to HNO_3 and then to aerosol nitrate. Likewise, the oxidation of SO_2 can occur via daytime sunlight- and VOC-driven gas phase reactions as well as aqueous-phase reaction with dissolved oxidants such as H_2O_2 and ozone. The complexity in formation is a result of the competing pathways and potentially limited reactant availabilities at many of the steps in the oxidation chemistry.

As a group, the secondary inorganic species (nitrate, sulfate, and ammonium) can account for up to 70% of $PM_{2.5}$ mass and up to 50% of PM_{10} mass in extreme wintertime pollution events in California's San Joaquin Valley (SJV). These species represent such a large portion of the PM that it is essential to characterize the factors influencing and, especially, limiting their formation. The detailed aerometric data collected during the measurement phase of CRPAQS provide an opportunity to advance the scientific understanding of these factors in general and, specifically, winter air pollution episodes in the SJV. A descriptive and interpretive data analysis study has been designed to address the following secondary formation-related questions:

1. Where and when do precursors (VOC, NO_x, NH_3, HNO_3, and SO_2) limit the formation of secondary sulfates and nitrates?
2. How is NO_x oxidized to nitric acid under clear sky versus cloudy/foggy conditions?
3. How much ozone and precursor species are above the valleywide layer and how much gets into the mixed layer?

The answers to these questions are important for understanding secondary aerosol problems and for selecting effective control strategies to reduce wintertime episodic PM levels in the region. The results of the proposed analyses are likely to be important for refining the conceptual model and for specifying the chemical and physical processes that need to be included in the atmospheric models that are used to model these data and candidate emission control strategies.

Scope of Work

We plan to focus on the factors influencing nitrate because we believe the nitrate issue is much more relevant to air resource management questions in the SJV than sulfate. Based on our review of ambient SO_4 data and limited SO_2 data for the past few years, it is clear that reducing SO_2 emissions to very low levels in California has been effective in limiting ambient sulfate concentrations.

The database for the analysis in Task 6.2 will be the same as that used for Task 6.1, with additional surface weather observations (sky cover and cloud ceiling height). The analysis of the factors influencing nitrate will be divided into five elements.

1. We will conduct exploratory analysis of indicator ratios for the gas-phase chemistry. We will examine the spatial and temporal variations in VOC/NO_x ratios, VOC reactivity, NO/NO_2 ratios, NO/NO_y ratios, HNO_3/NO_y ratios, PAN/NO_y ratios, and $O_3/(NO_y\text{-}NO)$ in order to characterize urban-versus-rural, fresh-versus-aged, cool-versus-warm, and winter-versus-summer photochemical characteristics that influence the overall rate of NO_x oxidation and HNO_3 formation.
2. We will stratify the indicator ratios by sky clearness, distinguishing clear sky conditions from cloudy, hazy, or foggy conditions as indicated by routine surface weather observations. The influence of variations in solar radiation intensity is likely to be evident in the NO/NO_y ratios and HNO_3/NO_y ratios and in the ozone concentrations.
3. We will specifically look for nighttime conditions with NO_2 and ozone present and with no NO present, which are believed to be the conditions under which NO_2 is converted to

HNO_3 via the nighttime mechanism. We hypothesize this mechanism is important aloft in the SJV, in rural areas, and in the foothills. We will compare data from the Sierra Nevada Foothills and Angiola sites with data from the Fresno and Bakersfield sites to characterize differences, if they exist.

4. Although there is no aircraft ozone or precursor data in the winter period, we can use the Sierra Nevada Foothills site to gauge ozone and precursor levels above the valley floor. By comparing foothill ozone and precursor levels with those various valley sites, the differences can be quantified. Using the windfields and mixing heights developed in Task 5.2, we can evaluate the likely amount of aloft and valley-air mixing in selected cases and interpret the roles and importance of ozone and precursors aloft in the overall chemistry in the valley.
5. We will scrutinize the HNO_3, NH_3, NO_3, NH_4, Na, and SO_4 aerosol data to see when and where nitrate levels are limited by HNO_3 versus NH_3. The data will also be stratified by temperature/RH regimes because they are important thermodynamically for gas-aerosol partitioning. Earlier data suggest aerosol nitrate is more frequently limited by HNO_3 production than by NH_3 levels in the SJV (Kumar et al., 1998). We anticipate that the large network of CRPAQS stations will allow us to find situations that are ammonia-limited, if they exist. We will account for the influence of Na and SO_4 in this analysis, but it is likely that neither of these components will be abundant enough to significantly influence nitrate levels.

We will prepare a manuscript describing the methods and results of analyses carried out under Task 6.2. This manuscript may cover more than one task. Presentation material will be prepared that incorporates the manuscript and additional tables, figures, and discussion items. The results will be presented at a west coast conference, such as the American Aerosol Association Research Conference scheduled for fall 2003.

Time Line

The schedule for this work depends on the availability of the overall CRPAQS data set which we assume will be available in early 2003. After we are notified that the database and documentation are available, there will be a two-month period during which the aerometric database will be assembled and reviewed. Analysis of these data will occur during the following two months. Preparation of the manuscript and presentation material will occur during the final two-month period. We anticipate that this six-month effort will occur in February–July of 2003.

Schedule of Deliverables

Deliverable	Deliverable Due Date
Final work plan	January 2003
Progress reports	Monthly
Draft manuscript	August 31, 2003
Final manuscript	September 30, 2003

Description of Deliverable(s)

The deliverables for this task consist of a final work plan; monthly progress reports that describe the technical progress, how unexpected problems are being handled, and budget expenditures; and the manuscript that describes the methods and results of analyses carried out under this task.

ARB Staff Assigned to this Task

The ARB Project Manager assigned to this Task is:

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STI Staff Assigned to this Task

The STI Project Manager is Lyle R. Chinkin. The STI Task Manager is Fred Lurmann.

Percentage of Work, Data Products to Be Performed/Delivered by ARB

None required.

Software and Models to Be Used by STI

Inorganic thermodynamic models such as SCAPE2 and AIM.

Models, Reports, or Other Data to Be Supplied to STI by ARB

None required.

References

Kumar N., Lurmann F.W., Pandis S., and Ansari A. (1998) Analysis of atmospheric chemistry during 1995 integrated monitoring study. Report prepared for the San Joaquin Valleywide Air Pollution Study Agency, c/o the California Air Resources Board, Sacramento, CA by Sonoma Technology, Inc., Petaluma, CA, STI-997214-1791-FR, July.